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(CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR. CHEMICAL LABORATORY OF HARVARD UNIVERSITY.)

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## THE ANALYSIS OF SILICON TETRACHLORIDE AND TETRABROMIDE.

By Gregory P. Baxter, Philip F. Weatherill and Edward W. Scripture, Jr.

*(Continued from page 3 of cover.)*

## VOLUME 58.

1. AMES, A. JR., PROCTOR, C. A., and AMES, BLANCHE.— Vision and the Technique of Art. pp. 1–47. 28 pls. In press.
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5. BRIDGMAN, P. W.— The Compressibility of Thirty Metals as a Function of Pressure and Temperature. pp. 163–242. January, 1923. $1.70.
6. BAXTER, GREGORY P., WEATHERILL, PHILIP F. and SCRIPTURE, EDWARD W., JR.— A Revision of the Atomic Weight of Silicon. The Analysis of Silicon Tetrachloride and Tetrabromide. pp. 243–268. February, 1923. $.75.

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### Introduction.

At the present time the atomic weight of silicon depends largely upon the analysis of the chloride and bromide of this element. Pelouze [1] and Dumas [2] compared the tetrachloride with silver, while Schiel [3] determined the silver chloride obtained from the same substance. Thorpe and Young [4] converted the tetrabromide to silica, and Becker and Meyer [5] used a similar method with the tetrachloride. Two determinations of the density of silicon tetrafluoride have been made by Jaquerod and Tourpaian [6] and by Germann and Booth.[7] The results of all these determinations have been collected and recalculated by F. W. Clarke [8] and are summarized in the following table.

| | | Atomic Weight of Silicon |
|---|---|---|
| Pelouze | $SiCl_4$ : 4 Ag | 28.37 |
| Dumas | $SiCl_4$ : 4 Ag | 28.08 |
| Schiel | $SiCl_4$ : 4 AgCl | 27.95 |
| Thorpe and Young | $SiBr_4$ : $SiO_2$ | 28.38 |
| Becker and Meyer | $SiCl_4$ : $SiO_2$ | 28.23 |
| Jaquerod and Tourpaian | Density $SiF_4$ | 28.50 |
| Germann and Booth | Density $SiF_4$ | 28.31 [9] |

1 Pelouze, Compt rend., **20**, 1047 (1845).
2 Dumas, Ann. Chem. Pharm., **113**, 31 (1860).
3 Schiel, Ann. Chem. Pharm., **120**, 94 (1861).
4 Thorpe and Young, J. Chem. Soc., **51**, 576 (1887).
5 Becker and Meyer, Z. anorg. Chem., **43**, 251 (1905); **47**, 45 (1905).
6 Jaquerod and Tourpaian, J. chim. phys., **11**, 28, 269 (1913).
7 Germann and Booth, J. Phys. Chem., **21**, 81 (1917).
8 Clarke, Memoirs of the Nat. Acad. Sci., Vol. XVI, No. 3. The Constants of Nature. Part V. A Recalculation of the Atomic Weights. 4th Ed., p. 222 (1920). See also the discussion by Brauner in Abegg's Handb. d. anorg. Chem., Vol. III, Pt. 2, 284 (1909).
9 Calculated by Clarke.

From these figures by the method of least squares Clarke computes the mean, 28.25, but calls attention to the uncertain nature of this value and to the desirability of new determinations of the constant in question.

In spite of the small percentage of silicon in the chloride and bromide, 16.5 and 8.6 respectively, so that the experimental error is magnified six and twelve times in calculating the atomic weight of silicon from the results of the analyses, on the whole these two substances seem to offer marked advantages for the purpose over any other compounds of silicon. Chief of these are the ease both of preparation and purification by distillation, and of analysis by comparison with silver.

A brief account of our preliminary experiments with silicon tetrachloride was published not long ago.[10] These experiments point to the value 28.11 for the atomic weight of silicon. Our subsequent experiments with both the chloride and bromide confirm the conclusion that silicon possesses an atomic weight lower than has been supposed, and indicate a value 28.06, which is even lower than the result of the preliminary experiments.

## Purification of Materials.

*Water.* Ordinary distilled water was twice redistilled, once from alkaline permanganate and once from very dilute sulfuric acid. The condensers were block tin tubes, fitted to Pyrex flasks with constricted necks, which served as stills. The connection was made by a water seal, no cork or rubber being used. The water was collected in Jena flasks, generally just previous to use.

*Nitric Acid.* Concentrated C. P. nitric acid was distilled through a quartz condenser, the first two-thirds as well as the last tenth being rejected.

*Sodium Hydroxide.* The best commercial material was dissolved and the greater part of the carbonate was precipitated with barium hydroxide. The supernatant solution was centrifuged until clear and then evaporated to crystallization in a platinum dish. Centrifugal drainage of the crystals in platinum Gooch crucibles [11] was followed by rinsing with a small quantity of water and a second drainage. Recrystallization in the same way was continued until the mother

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10 Baxter, Weatherill and Holmes, Jour. Am. Chem. Soc., **42**, 1194 (1920).
11 Baxter, Jour. Am. Chem. Soc., **30**, 286 (1908).

liquor was free from chloride. This required from three to six crystallizations according to the quality of the original material.

Two other specimens of hydroxide were made by combining barium hydroxide and sodium carbonate, after both substances had been crystallized until free from chloride. The resulting solution was then evaporated to crystallization, and the product was recrystallized.

*Bromine.* This material had been purified by Mr. A. F. Scott according to the method which has been frequently used at Harvard.[12] Crude bromine was first distilled from aqueous potassium bromide in order to remove chlorine. Next one-fourth of the product was converted to potassium bromide by means of recrystallized potassium oxalate, and the remaining three-fourths of the bromine was distilled from solution in this potassium bromide. All the product was then converted to potassium bromide by means of potassium oxalate, and the potassium bromide was fused in a platinum dish with enough recrystallized potassium permanganate to oxidize all organic matter. In order to obtain bromine the purified potassium bromide was dissolved in a solution of pure sulfuric acid. The excess of potassium permanganate contained by the salt caused a small quantity of bromine to be liberated. This bromine was removed by distillation since it might have contained a trace of iodine. Enough pure permanganate to liberate the greater portion of the bromine was then added, and the bromine was distilled into a receiver cooled with ice. In this last step the bromine received a third distillation from a bromide. The product was separated from the water, dried with resublimed phosphorus pentoxide and once redistilled.

*Silver.* This substance was prepared by standard methods. These consisted in brief of the following processes: double precipitation as chloride, followed by reduction with alkaline sugar solution, fusion of the metal on charcoal, solution and reprecipitation with ammonium formate, fusion on pure lime, electrolytic transport, fusion on pure lime in hydrogen, etching, drying in a vacuum at 500°. Recent work by Baxter and Parsons [13] and Baxter [14] as well as earlier work have shown that these processes yield a product of adequate purity.

*Nitrogen.* This gas was prepared by the Wanklyn process. Air was charged with ammonia and passed over hot copper catalyst. The

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12 Baxter, Moore and Boylston, These Proceedings, **47**, 585 (1912); Jour. Amer. Chem. Soc., **34**, 1644 (1912); Baxter and Grover, Jour. Amer. Chem. Soc., **37**, 1029 (1915).

13 Baxter and Parsons, Jour. Amer. Chem. Soc., **44**, 577 (1922).

14 Baxter, Ibid., **44**, 591 (1922).

excess of ammonia was removed by wash bottles containing dilute sulfuric acid. Hydrogen resulting from catalytic decomposition of the ammonia was next burned with hot copper oxide, and the gas was then purified and dried by silver nitrate solution, sodium hydroxide, concentrated sulfuric acid and phosphorus pentoxide. Finally last traces of oxygen were absorbed by hot copper oxide. The apparatus, which was constructed entirely of glass, is described in detail by Baxter and Grover.[15]

### The Preparation of Silicon Tetrachloride.

The silicon tetrachloride was prepared by the action of chlorine on silicon, and was purified by distillation in exhausted glass vessels without exposure to air or moisture. Moisture was particularly to be avoided because of the decomposition products resulting from hydrolysis, i.e., silicic acid, silicon oxychlorides and hydrochloric acid. Because in preparing the chloride it was impossible entirely to avoid exposure to moist air, the process of purification was adapted for the removal of these impurities. In addition to the above impurities, the following were to be expected and provided for: silicon hexachloride and octachloride, titanium tetrachloride and carbon tetrachloride, the last two resulting from impurities of carbon and titanium in the silicon. Fortunately the boiling points of all the impurities are sufficiently far removed from that of silicon tetrachloride to lead to the expectation that they would be readily removed by fractional distillation. So far as can be told this proved to be the case. In the following table are given the boiling points of the impurities in question.

| | bpt. | | bpt. |
|---|---|---|---|
| $SiCl_4$ | 58° | HCl | −83° |
| $Si_2Cl_6$ | 146–148° | $CCl_4$ | 76.5° |
| $Si_3Cl_8$ | 200–215° | $TiCl_4$ | 136° |
| $Si_2OCl_6$ | 137–138° | | |

Several specimens of the tetrachloride were prepared, differing chiefly in the method and extent of the fractionation. One lot was purchased from the General Electric Company. This had been made from silicon and chlorine, and had been rectified. Our own preparations were made as follows: Dry chlorine was passed over silicon in a hard glass tube heated to redness, and the product was condensed. The chlorine was drawn from a large tank which served for all the prepara-

[15] Baxter and Grover, Jour. Amer. Chem. Soc., **37**, 1037 (1915).

tions, and was purified and dried by passing through two towers filled with beads wet with water, then three similar towers containing concentrated sulfuric acid, and finally through a tube containing resublimed phosphorus pentoxide. The silicon, in the form of a coarse powder, was contained in a hard glass tube which could be electrically heated and which was inclined toward the large glass bulb cooled with ice which served as condenser. Connection with both the chlorine purifier and the condenser was made with dry ground joints, and all other connections in the apparatus were made with glass seals, except

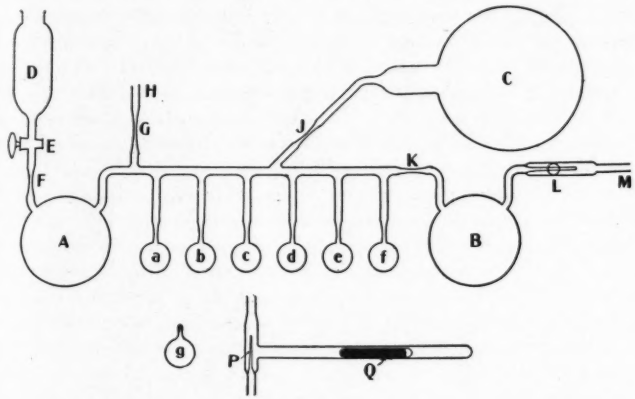


FIGURE 1.

that between the chlorine tank and the purifying apparatus, which consisted of a very short rubber connector. Since the reaction is highly exothermic, comparatively little heat was required.

The material obtained from the General Electric Company was a clear colorless liquid. The initial product of our own process was a dark colored liquid containing both dissolved and suspended ferric chloride, titanium chloride, chlorine, hydrochloric acid and probably some or all of the other impurities mentioned above.

Sample I was a mixture of General Electric Company product with some of our own. Sample II consisted entirely of General Electric Company material. Samples III and IV were two separate preparations of our own.

The fractional distillation of the first three samples was effected in apparatus of the general type shown in Figure 1. This apparatus

resembles closely that used by Baxter, Moore and Boylston [16] for the preparation of phosphorus tribromide, by Baxter and Moore [17] for the preparation of phosphorus trichloride and by Baxter and Starkweather [18] for the preparation of tin tetrachloride. Two bulbs, *A* and *B*, of about 300 cc. capacity serve as stills or receivers. The separatory funnel *D* is employed during the introduction of the material. The flask *C* of one liter or more capacity is an expansion reservoir for removing permanent gases. The small bulbs *a*, *b*, *c*, etc. are fractionating bulbs. The various parts of the apparatus may be disconnected by sealing the capillaries *F*, *G*, *J*, *K*, etc. By means of the special joint *L*, the final receiver *B* may subsequently be connected with another similar system without exposure to air or moisture.

The special joint *L* is shown on a large scale in Figure 1. The sealed-in capillary *P* is closed at the end and is scratched with a file at several points to facilitate breaking. To break the joint the closed tube of glass weighted with mercury *Q* is allowed to strike the capillary with some force. Bruner and Bekier,[19] Briscoe and Little [20] and Baxter and Starkweather [18] used a similar device, while Richards and Craig [21] employed a magnetic hammer instead of one operated by gravity.

First the stopcock *E* is made tight by rings of grease on the ends of the cock and by pouring a small amount of mercury into the separatory funnel *D*. The whole apparatus is next exhausted through *H* and the capillary *G* is sealed. Next *D* is filled with silicon tetrachloride and the mercury and nearly all the tetrachloride are admitted to *A*. Again a small amount of mercury is poured into *D* to seal the stopcock and as soon as possible the capillary *F* is sealed. By sealing off the globe *C* at *J* a large part of the permanent gases originally dissolved in the liquid chloride can be removed. The more volatile fractions of material are condensed in some of the small bulbs, *a*, *b*, *c*, by means of liquid air or carbon dioxide-alcohol mixture, and are sealed off. Then the main portion of material is distilled into *B* which is sealed off at *K*, leaving the least volatile fraction in *A*. Subsequently, if desired, the residue in *A* can be distilled into *d*, *e*, *f*, for examination.

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16 Baxter, Moore and Boylston, These Proceedings, **47** 590 (1912); Jour. Amer. Chem. Soc., **34**, 263 (1912); Z. anorg. Chem., **74**, 365 (1912).

17 Baxter and Moore, Orig. Com. Eighth Internal. Cong. Appl. Chem., Vol. II, 21 (1912); Jour. Amer. Chem. Soc., **34**, 1644 (1912); Z. anorg. Chem., **80**, 189 (1913).

18 Baxter and Starkweather, Jour. Amer. Chem. Soc., **42**, 907 (1920).

19 Bruner and Bekier, Z. f. Elektrochem, **18**, 369 (1912).

20 Briscoe and Little, Jour. Chem. Soc., **105**, 1321 (1914).

21 Richards and Craig, Jour. Amer. Chem. Soc., **41**, 131 (1919)

A new distillation system can now be sealed on at $M$ and the process repeated.

*Sample I.* All the details of the fractionation of Sample I are shown in Figure 2. The chloride was freed from suspended material by filtration through glass wool and was admitted to the exhausted bulb $A$ together with several cubic centimeters of mercury. After standing for a week with occasional shaking, in order to remove the excess of chlorine as mercurous chloride, three small fractions, $a$, $b$, $c$, were removed and all but about one fifth the original chloride was distilled into $B$. From $B$ about four fifths of the product was dis-

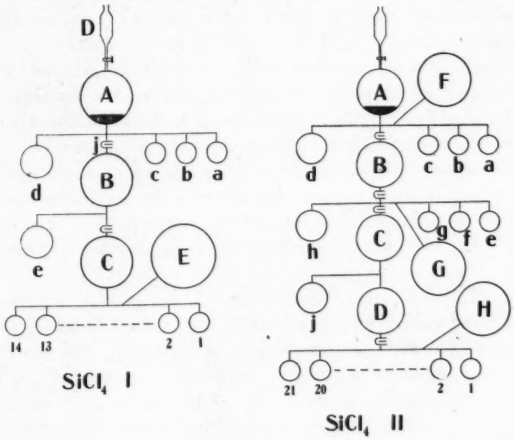


FIGURE 2.

tilled into $C$, after sealing off the liter reservoir $E$, and finally all the material was collected in fourteen small bulbs, 1–14. The appearance of a bulb sealed off for analysis is shown at $g$ (Fig. 1). In the figures, special joints are represented as at $j$, expansion reservoirs as at $E$, more volatile fractions to the right of the center, $a$, $b$, $c$, less volatile fractions to the left of the center, $d$, $e$. The volumes of the fractions are indicated roughly by the size of the circles. Fractions 3, 6, 9 and 12 were analyzed.

*Sample II.* Figure 2 shows diagrammatically the fractionation of Sample II. After standing over mercury for some time, three small light fractions, $a$, $b$, $c$, were removed with liquid air and the greater

part of the remainder was distilled into *B* leaving a residue *d* of about one-sixth. In spite of the use of the expansion reservoir *F*, distillation refused to begin when the bulbs, *a*, *b*, *c*, were cooled with carbon dioxide-alcohol mixture. Since, however, liquid air was effective in starting the distillation, and since thereafter carbon dioxide-alcohol refrigerant proved sufficient, it seems likely that hydrochloric acid gas was responsible for the delay. In the next two steps the expansion reservoir *G* and three light fractions, *e*, *f*, *g*, were removed, and two residues *h* and *j* were rejected when the bulk of the material was distilled successively into *C* and *D*. From *D* all the remainder was collected in twenty one small bulbs, except for a residue of obviously less volatile oily material, amounting to a few tenths of a cubic centimeter. Of the final fractions, Nos. 1, 7, 13 and 20 were analyzed.

In order to discover whether the non-volatile residue was diminishing in quantity with successive distillations, residue *j* was transferred to an exhausted bulb without exposure to air and fractionally distilled. Here the last cubic centimeter, as in the case of the residue in *D*, consisted of a colorless oily liquid, which could be distilled by warming but which was obviously less volatile than the tetrachloride. In the preparation of Sample III it was found that a part of this material is titanium tetrachloride. The remainder is apparently higher chlorides of silicon.

*Sample III.* In preparing Sample III, the product of the reaction of chlorine on silicon was collected in the bulb *A* (Fig. 3) which was then connected with an efficient water pump. The liquid boiled vigorously under these conditions, so that a large part of the excess of chlorine and probably much of the hydrochloric acid were removed at the outset. Furthermore the boiling of the tetrachloride must have flushed out most of the air originally in the bulb. After removal of the light fractions, *a*, *b*, *c*, with liquid air, the bulk of the material was distilled into bulb *B*, containing mercury, and allowed to stand for four months. In each of the fourteen distillations of the main portion, a residue of several cubic centimeters was left in the still, and usually was collected as two or more fractions. Furthermore nine more volatile fractions were rejected in the first four distillations. The final product was collected in twenty one small bulbs, of which Nos. 1, 13, 16 and 21 were analyzed. From the point of view of quantity of material bulb 14 represents about the middle of this series.

In the first seven distillations the oily, less volatile residue observed in the preparation of Sample II appeared, in gradually decreasing proportions. Some of this material was found by qualitative testing

with hydrogen peroxide to contain titanium. The quantity of titanium contained in fraction *j* was very small, however, and none could be found in fraction *k*. Furthermore the amount found in fractions *d* and *e* seemed far too small to account for the quantity of less volatile residue, so that we are inclined to believe that a considerable portion of the residue consisted of higher chlorides of silicon.

*Sample IV.* Still a fourth sample of tetrachloride was purified as

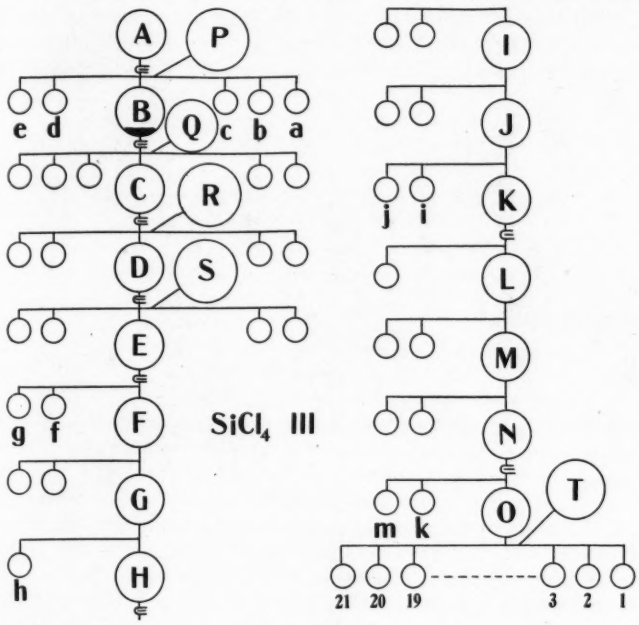


FIGURE 3.

described under the preparation of Sample II. Owing to the discovery of the less volatile residue in Sample II, the fractions originally obtained in this way were not analyzed. After the preparation of Sample III, however, Mr. A. F. Scott, who was engaged in the Coolidge Memorial Laboratory in the purification of boron trichloride by fractional distillation, found that a Hempel column could be conveniently employed in a distillation at low temperatures, provided the

column was chilled to a suitable temperature intermediate between that of the still and the condenser. Since it was a simple matter to apply this principle to the distillation of silicon tetrachloride, all of the fractions resulting from the first distillation, without regard to purity, together with a considerable number of rejected fractions obtained in

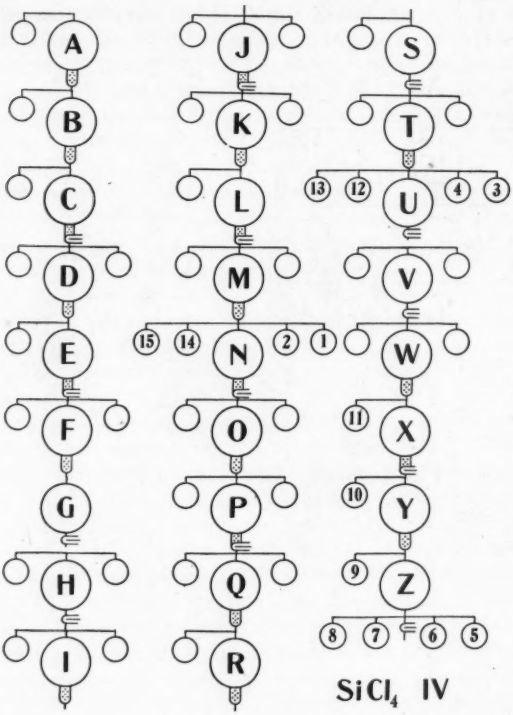


FIGURE 4.

the purification of Sample III, were combined in a large bottle by breaking the bulbs with a heavy glass rod, and the mixture was subjected to a new fractionation, as indicated in Figure 4.

The material was poured into bulb *A* through a glass funnel and the bulb, while immersed in hot water, was exhausted with an efficient

water pump, through a drying tube containing sodium hydroxide. The tetrachloride was allowed to boil vigorously for a short time, until several cubic centimeters had evaporated, together, we hoped, with much of the hydrochloric acid formed by exposure to the moisture of the air. Repeated distillation was then carried out with apparatus similar to that indicated in Figure 5. The Hempel column was cooled with ice and water, while the receiver was chilled with carbon dioxide-alcohol mixture. A continuous reflux action was evident in the Hempel column throughout the distillation. In each distillation a few cubic centimeters of residue were rejected. Furthermore, frequently at the end of a distillation the temperatures of still and receiver were re-

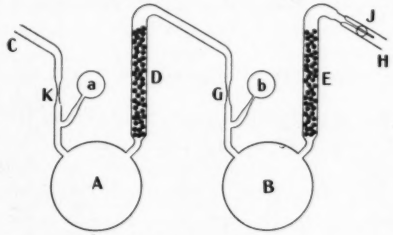


FIGURE 5.

reversed so that the most volatile material was largely condensed in the still. Sometimes the same effect was produced by inserting an additional large bulb in the train and condensing the most volatile material in this bulb before the next distillation.

After six distillations, one of the capillary connections in the apparatus was accidentally broken so that moist air was admitted. With as little exposure to the air as possible the chloride was introduced into bulb *H* and seven more distillations were carried out in the same way. In the last distillation the two most volatile fractions (1 and 2, Fig. 4) were collected for analysis, the main bulk of material was distilled into bulb *O* from bulb *N*, and the residue was collected in bulbs 14 and 15 for analysis.

Since the possibility of the existence of constant boiling distillates is always to be feared in fractional distillation, an effort was made to avoid or detect the effect of such a mixture by further distillation at a different pressure. To do this the still was immersed in warm water, the Hempel column was kept at about 5° and the receiver was sur-

rounded with ice and water. In the seventh distillation at the higher pressure the two most volatile fractions, 3 and 4, were collected for analysis, as well as the two least volatile fractions, 12 and 13 (Fig. 4).

Unfortunately at this point the apparatus was again opened to the air by the breakage of a capillary. Although the quantity of material was by this time much diminished, about 30 cc., the remainder was introduced into bulb *V* and the bulb thoroughly flushed out with tetrachloride vapor. Further fractionation at the lower pressure, using carbon dioxide-alcohol as refrigerant, yielded three residual fractions, 9, 10 and 11, while the remainder was collected in the four fractions, 5, 6, 7 and 8.

Sample I was purified by Dr. E. O. Holmes, Jr., Samples II and III by Dr. Weatherill, and Sample IV by Mr. Scripture.

## The Analysis of Silicon Tetrachloride.

After being weighed the bulb containing silicon tetrachloride was broken under an excess of sodium hydroxide and the glass was collected and weighed. The solution was diluted to considerable volume and made acid with nitric acid, and then was precipitated with a solution of a weighed very nearly equivalent amount of pure silver. The point of exact equivalence between chloride and silver was then found with the assistance of a nephelometer.

The bulb of material selected for analysis was soaked first in cleaning solution, then for several days in pure water. Sometimes the capillary was slightly scratched with a file. Next the bulb, suspended in a platinum wire basket, was weighed under water of known temperature. After being dried with a clean, nearly lintless cloth, the bulb was allowed to remain at least over night in a desiccator containing fused potassium hydroxide. Weighing by substitution followed, and the temperature, pressure, and humidity of the balance case were observed at the same time. From the loss in weight under water the volume of the bulb was computed, and then from the atmospheric conditions the buoyant effect of the air on the bulb. In weighing the fractions of Sample IV, the atmospheric density was found from the weight of a sealed, standardized globe.[22]

A solution of about fifty per cent excess of the quantity of pure sodium hydroxide (purified as described on page 247) necessary to react completely with the tetrachloride was filtered into a heavy walled 2

[22] Baxter, Jour. Amer. Chem. Soc., **43**, 1317 (1921).

liter conical Jena flask, which was provided with a particularly well ground glass stopper. The volume of the sodium hydroxide solution varied from 200 to 400 c.c. according to the weight of the tetrachloride sample. The bulb was introduced and after thoroughly wetting the walls and stopper of the flask with the alkali, the bulb was broken by shaking the flask. The fog produced on breaking of the bulb apparently disappeared after fifteen or twenty minutes, but the flask was not opened for several hours, in order to make certain that no silicon tetrachloride or hydrochloric acid vapor was lost.

The solution was always perfectly clear, although in a few instances silicic acid separated in the end of the capillary of the bulb. This difficulty remedied itself in some instances, for on standing the silicic acid dissolved in the alkaline solution. In others, this process was assisted by breaking the capillary with a blunt rod. In no case was an analysis continued until all traces of such a deposit had disappeared, and two experiments were abandoned because of undissolved silicic acid in the capillary.

Next the contents of the flask were diluted to 700–800 cc. and were filtered through a quantitative filter into a glass-stoppered precipitating flask or bottle. The glass fragments were washed by decantation several times and were collected on the filter, and finally the filter paper was charred and the residue burned in a platinum crucible at as low a temperature as possible so as to avoid the danger of volatilizing alkali from the glass.

In order to find out whether it is possible to wash the filter free from sodium silicate and silicic acid, several blank experiments were carried out in which a similar alkaline solution of silicon tetrachloride was filtered in the same way through a quantitative filter, and after thorough washing with water the filter was burned. In still other experiments a weighed empty bulb similar to those used in collecting the silicon tetrachloride for analysis, but open to the air, was broken in the silicate solution and the glass fragments were collected and determined as above. In all these experiments the ash of the paper was found to be slightly in excess of the weight to be expected.

| | Excess mg. |
|---|---|
| Without glass bulb | 0.21 |
| | 0.15 |
| | 0.16 |
| With glass bulb | 0.14 |
| | 0.35 |
| Average | 0.20 |

In experiments where the foregoing method of determining the glass was employed (Series I and II) a negative correction of 0.20 mg. has therefore been applied.

Since we found that silicate solutions, of the concentration obtained in these analyses, when acidified with one per cent nitric acid remain clear indefinitely, the experiment was tried of washing the glass fragments and the filter paper with nitric acid of this concentration. Somewhat to our surprise not only did the excess in weight of the ash disappear, but a slight deficiency was found. Since this deficiency was practically the same whether or not a glass bulb was involved, it is apparent that some of the mineral constituents of the filter are extracted by either the alkaline silicate or the nitric acid.

The following table gives the results obtained in blank experiments in which one per cent nitric acid was used as washing liquid.

| | Deficiency mg. |
|---|---|
| Without glass bulb | 0.08 |
| | 0.08 |
| | 0.12 |
| | 0.01 |
| | 0.09 |
| With glass bulb | 0.13 |
| | 0.01 |
| | 0.02 |
| Average | 0.07 |

The method of filtering the sodium hydroxide solution of the silicon chloride through the filter and then washing the glass and filter with one per cent nitric acid was followed in all the analyses of Series III, and in Analyses 21 to 25 of Series V. In these experiments an average positive correction of 0.07 mg. was applied to the weight of the glass before subtracting the weight of the filter ash, 0.11 mg.

In all the analyses of Series IV and Analyses 26, 27 and 28 of Series V, the glass was washed with one per cent nitric acid, but a different variety of filter was employed. Blank experiments with these filters gave the following results:

| | Excess mg. |
|---|---|
| Without glass bulb | 0.05 |
| | 0.03 |

| | Excess mg. |
|---|---|
| With glass bulb | 0.04 |
| | 0.04 |
| | −0.04 |
| | −0.04 |
| | 0.09 |
| | 0.08 |
| Average | 0.03 |

In these experiments a negative correction of 0.03 mg. was applied to the weight of the glass.

The filtrate from the glass was then made acid by adding, in the form of 1 normal solution, a quantity of nitric acid equivalent to the sodium hydroxide used. Since a fifty per cent excess of sodium hydroxide was used, and since four ninths was changed to sodium chloride, after the addition of the nitric acid the total acidity was not far from 0.1 normal. This could do no harm, however, for Hönigschmid [23] has found that even three normal nitric acid liberates no hydrochloric acid or chlorine from a similar quantity of potassium chloride.

From the corrected weight of silicon tetrachloride the weight of silver necessary to precipitate the chloride was computed. This quantity was weighed out, chiefly in the form of a very few large buttons, the final adjustment being made with small electrolytic crystals. After careful solution of the silver in chloride-free nitric acid and elimination of nitrous acid, in a flask provided with a spray trap in the form of a column of bulbs ground into the neck, the solution was diluted to tenth normal concentration or less, and then was added slowly with constant agitation to the chloride solution contained in a glass stoppered flask or bottle. The mixture was allowed to stand for several days with occasional shaking, before testing for excess of chloride or silver in a nephelometer. If an excess of either was found, the deficiency of the other was made up by adding hundredth normal solution until the endpoint had been reached. Even then the solutions were allowed to stand for some weeks longer with occasional shaking in order to allow included or occluded material to be extracted from the precipitate. Only slight changes were ever produced by this standing.

The manipulations of precipitation and testing of the solutions were

[23] Hönigschmid, Z. Elektrochem., **26**, 403 (1920); Ber. d. d. chem. Gesell., **54**, B, 1873 (1921).

always carried out in ruby light. In using the nephelometer all the precautions noted by Richards and Wells [24] were observed, such as preparing the comparison tubes under as nearly as possible identical conditions of temperature, concentration, and time, allowing the tubes to come to constant ratio by standing for an hour or more, and taking the average of several readings of each ratio.

## The Preparation of Silicon Tetrabromide.

To prepare silicon tetrabromide, dry nitrogen saturated with pure bromine at a temperature not far below the boiling point of bromine was passed over silicon at red heat in an all-glass apparatus very similar to that used for preparing the tetrachloride. Since the layer of silicon was long, very little bromine passed through the reaction tube into the receiver. About six hundred grams were secured in the single preparation which was made.

The bromide was then subjected to fractional distillation for removal of the impurities which experience with the chloride led us to expect. Since the boiling point of the tetrabromide, 153°, is far higher than that of the chloride, the distillations were carried out by heating the still instead of by cooling the receiver. Furthermore, Hempel columns were employed in most of the distillations.

The boiling points of the probable volatile impurities to be expected are as follows:

| | bpt. | | bpt. |
|---|---|---|---|
| $SiBr_4$ | 153° | HBr | −69° |
| $Si_2Br_6$ | 240° | $CBr_4$ | 190° |
| | | $TiBr_4$ | 230° |

Chlorobromides were not to be feared, since the bromine used was chlorine-free.

The general type of apparatus used in the distillations is shown in Figure 5. The material in the bulb *A*, which has been filled from a previous distillation and sealed off at *K*, is warmed in a water bath and is distilled through the Hempel column *D* into the bulb *B*, which is cooled with ice, leaving a residue of a few cubic centimeters in *A*. The bulb *A* is then separated by sealing the capillary *G*. *B* terminates in a special joint *J* through which it may be attached to another similar system. The residues left in *A* and *B* may then be distilled into the small bulbs *a* and *b* by inclining the bulbs to a suitable angle. The complete course of the tetrabromide distillation is shown in Figure 6.

[24] Richards and Wells, Amer. Chem. Jour., **31**, 235 (1904); **35**, 510 (1906).

After the material had been collected in bulb $A$, a considerable amount of mercury was added and, with the bulb and contents nearly at 100°, the bulb was exhausted through a drying tube by a very efficient water pump. The liquid boiled vigorously so that a large part of the excess

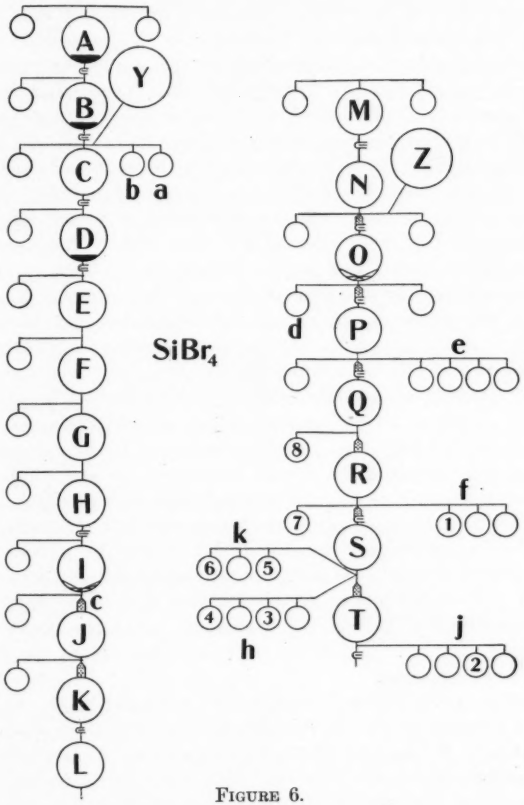


FIGURE 6.

of bromine evaporated, together with tetrabromide vapor. The air must have been thoroughly flushed out by this boiling. Probably a large portion of hydrobromic acid formed by hydrolysis was removed at the same time. The bulb $A$ was sealed off while the pump was operating. Upon shaking the bulb $A$, after cooling, the mercury

combined with the greater part of the bromine. Bulb *B*, also containing mercury, was then attached and exhausted, and the material poured from *A* to *B*, where it was again shaken with fresh mercury. Connection was now made with the system *C*, *Y*, *a*, *b*, First the two liter expansion flask *Y* was sealed off. Two small fractions *a* and *b* were next removed by cooling with liquid air while *B* was warmed, and all but about 6 cc. was distilled into *C* and sealed off. The material in *a* and *b* was colored yellow, owing doubtless to free bromine. The main fraction in *C* also was slightly colored, as well as the residue in *B*. Another distillation into *D* which also contained mercury followed, and then a series of five distillations into *I*. In all these distillations a slight cloudiness persisted in the main body of material. Since we feared that this might be a bromide of mercury vaporizing with the silicon tetrabromide, several pieces of bright copper wire were placed in *I*. These pieces of wire were slightly discolored during the distillation from *I*, but since a fractionating column, as indicated at *c*, was used for the first time in the next distillation, it is uncertain whether the copper or the column was responsible for the great improvement in the appearance of the distillate; for from this point on it remained perfectly clear and colorless.

After distillation into the bulb *L*, the accidental breaking of a capillary admitted air and consequently a small amount of moisture to the tetrabromide. With as little exposure to air as possible the material was poured from *L* into a suitably prepared bulb *M* and again exhausted as before. After distillation into *N*, but before sealing off the connection to *M*, *N* was warmed and *M* was cooled so that several cubic centimeters were distilled back into *M*. This procedure is indicated in Figure 6 as if a light fraction had actually been collected from *N*. A similar procedure was followed in the next distillation.

The contents of the bulb *d*, which contained the heavy fraction remaining after the distillation from *O*, were tested for titanium, with a negative result.

Although a few pieces of copper wire were used in *O*, to remove a trace of bromine which was formed apparently by the exposure to the air in *L* and *M*, the first of the four light fractions removed from *P* had a slight yellow color; the remaining three were colorless.

After about half the material had been distilled from *S* to *T*, four small samples were collected as indicated at *h*, the remainder was distilled into *T*, leaving a residue which was collected in three portions, indicated at *k*.

The samples analyzed were, 1, the least volatile of three light fractions taken from *R*, 2, the second most volatile fraction from *T*,

3 and 4, middle fractions from *S*, 5 and 6, the least volatile material from *S*, 7, the residue left from the distillation from *R* and 8, a similar residue from *Q*.

### The Analysis of Silicon Tetrabromide.

The analysis of silicon tetrabromide was carried out almost exactly as described in the case of the tetrachloride. The glass of the bulb was washed with one per cent nitric acid and allowance made for reduction of the weight of the filter ash as described on page 258. When the end point of the comparison had been reached, the portions tested with silver and bromide solutions remained almost perfectly clear. This indicates the absence of appreciable amounts of chloride, and is to be expected in view of the pains taken to remove chlorine from the bromine.

Weighings were made on a No. 10 Troemner balance, sensitive to 0.02 mg. with a load of fifty grams. The beam was graduated to 0.05 milligram and the 5 mg. rider was used to determine all quantities larger than this, interpolation from the zero points being employed for amounts less than 0.05 milligram.

The weights were of gold plated brass, except the fractional weights, and were compared by the Richards [25] method.

All weighings were by substitution. In the case of the bulb and the silver, the weights were substituted for the object weighed. In the case of the glass, the crucible was substituted for a similar counterpoise.

Impure radium bromide was kept in the balance case to prevent electrostatic effects.

Vacuum corrections were applied as follows:

| Weights | Density | Vacuum Correction per gram |
|---|---|---|
| Weights | 8.3 | |
| Ag | 10.49 | −0.000031 |
| glass | 2.5 | +0.000335 |
| air | 0.001293 | |

at 0° and 760 mm.

Humidity was read on an accurate hair hygrometer.

The analyses of Series I, II, III, and analyses 21, 22, 23, 24 and 25 of Series V were performed by Dr. Weatherill. All analyses of Series IV and analyses 26, 27 and 28 of Series V were performed by Mr. Scripture.

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[25] T. W. Richards, Jour. Amer. Chem. Soc., **22**, 144 (1900).

TABLE I.

$SiCl_4 : 4\,Ag$.

SERIES I. Sample I.

| Number of Analysis | Fraction of $SiCl_4$ | Ag = 107.880 Weight of $SiCl_4$ in vacuum gm. | Weight of Ag in vacuum gm. | Weight of Ag added or subtracted in solution gm. | Corrected Weight of Ag in vacuum gm. | Cl = 35.457 Ratio $SiCl_4 : 4\,Ag$ | Atomic Weight of Silicon |
|---|---|---|---|---|---|---|---|
| 1 | 12 | 10.43530 | 26.47403 | +0.02120 | 26.49523 | 0.393856 | 28.129 |
| 2 | 3 | 5.97853 | 15.17909 | +0.00395 | 15.18304 | 0.393764 | 28.089 |
| 3 | 9 | 8.79053 | 22.31981 | +0.00150 | 22.32131 | 0.393818 | 28.112 |
| 4 | 6 | 6.83524 | 17.35557 | +0.00060 | 17.35617 | 0.393822 | 28.114 |
| | | | | | Average | 0.393815 | 28.111 |
| | | | SERIES II. Sample II. | | | | |
| 5 | 7 | 5.68295 | 14.43153 | 0.00000 | 14.43153 | 0.393787 | 28.099 |
| 6 | 13 | 5.01510 | 12.73571 | 0.00000 | 12.73571 | 0.393783 | 28.097 |
| 7 | 1 | 3.73771 | 9.49172 | 0.00000 | 9.49172 | 0.393786 | 28.099 |
| 8 | 20 | 7.58979 | 19.27465 | −0.00590 | 19.26875 | (0.393891) | (28.144) |
| | | | | | Average, omitting Analysis 8 | 0.393787 | 28.099 |
| | | | SERIES III. Sample III. | | | | |
| 9 | 1 | 2.97268 | 7.54875 | +0.00065 | 7.54940 | 0.393764 | 28.089 |
| 10 | 21 | 2.49266 | 6.33002 | −0.00202 | 6.32800 | (0.393910) | (28.152) |
| 11 | 13 | 4.38690 | 11.14025 | +0.00065 | 11.14090 | 0.393765 | 28.090 |
| 12 | 16 | 4.23780 | 11.76180 | +0.00415 | 10.76595 | 0.393630 | 28.031 |
| | | | | | Average, omitting Analysis 10 | 0.393711 | 28.070 |
| | | | SERIES IV. Sample IV. | | | | |
| 13 | 1 | 6.32161 | 16.05564 | +0.00040 | 16.05604 | 0.393722 | 28.071 |
| 14 | 10 | 2.50810 | 6.37019 | +0.00040 | 6.37059 | 0.393700 | 28.061 |
| 15 | 4 | 6.30110 | 16.00486 | −0.00030 | 16.00456 | 0.393707 | 28.064 |
| 16 | 8 | 7.02208 | 17.83944 | −0.00410 | 17.83534 | 0.393717 | 28.069 |
| 17 | 11 | 4.14551 | 10.52927 | +0.00015 | 10.52942 | 0.393707 | 28.065 |
| 18 | 12 | 6.43140 | 16.33562 | −0.00010 | 16.33552 | 0.393707 | 28.064 |
| 19 | 14 | 6.17527 | 15.68345 | +0.00080 | 15.68425 | 0.393724 | 28.072 |
| 20 | 6 | 6.56940 | 16.68581 | −0.00010 | 16.68571 | 0.393714 | 28.068 |
| | | | | | Average | 0.393712 | 28.067 |

TABLE II.

$SiBr_4 : 4\,Ag.$

Series V.

Ag = 107.880 Br = 79.916

| Number of Analysis | Fraction of $SiBr_4$ | Weight of $SiBr_4$ in vacuum | Weight of Ag in vacuum | Weight of Ag added or subtracted in solution | Corrected Weight of Ag in vacuum | Ratio $SiBr_4 : 4\,Ag$ | Atomic Weight of Silicon |
|---|---|---|---|---|---|---|---|
| | | gm. | gm. | gm. | gm. | | |
| 21 | 1 | 6.29408 | 7.81228 | −0.00153 | 7.81075 | 0.805823 | 28.064 |
| 22 | 8 | 7.08409 | 8.78878 | +0.00164 | 8.79042 | (0.805888) | (28.093) |
| 23 | 2 | 8.75434 | 10.86317 | +0.00070 | 10.86387 | 0.805821 | 28.064 |
| 24 | 4 | 6.09639 | 7.56496 | +0.00070 | 7.56566 | 0.805797 | 28.054 |
| 25 | 5 | 5.89649 | 7.31704 | +0.00050 | 7.31754 | 0.805802 | 28.056 |
| 26 | 3 | 5.32962 | 6.61348 | +0.00050 | 6.61398 | 0.805811 | 28.060 |
| 27 | 7 | 5.87675 | 7.29263 | +0.00050 | 7.29313 | 0.805792 | 28.052 |
| 28 | 6 | 4.16665 | 5.17077 | −0.00010 | 5.17067 | 0.805824 | 28.065 |
| | | | | Average omitting Analysis 22 | | 0.805810 | 28.059 |
| | | | | Average of Series IV and V | | | 28.063 |

In the foregoing tables the analyses are arranged in the order in which they were carried out. A better comparison of the various fractions is obtained if the results are tabulated in the order of volatility. The following table gives the observed atomic weights in the order of decreasing volatility for the different chloride samples as well as for the bromide.

| $SiCl_4$ I | | $SiCl_4$ II | | $SiCl_4$ III | |
|---|---|---|---|---|---|
| Fraction | At.Wt. | Fraction | At.Wt. | Fraction | At.Wt. |
| 3 | 28.089 | 1 | 28.099 | 1 | 28.089 |
| 6 | 28.114 | 7 | 28.099 | 13 | 28.090 |
| 9 | 28.112 | 13 | 28.097 | 16 | 28.031 |
| 12 | 28.129 | 20 | 28.144 | 21 | 28.152 |

| $SiCl_4$ IV | | $SiBr_4$ | |
|---|---|---|---|
| Fraction | At.Wt. | Fraction | At.Wt. |
| 1 | 28.071 | 1 | 28.064 |
| 4 | 28.064 | 2 | 28.064 |
| 6 | 28.068 | 3 | 28.062 |
| 8 | 28.067 | 4 | 28.054 |
| 10 | 28.063 | 5 | 28.056 |
| 11 | 28.064 | 6 | 28.068 |
| 12 | 28.065 | 7 | 28.054 |
| 14 | 28.071 | 8 | 28.093 |

In the first three series, with the exception of Fraction 16, Series III, there is unmistakable evidence of slightly increasing atomic weight with decreasing volatility. It is especially noticeable that Fraction 12, Series I, Fraction 20, Series II, and Fraction 21, Series III, which were the third from the last, the next to the last and the last fractions respectively, all give values nearly alike and markedly higher than the others. As explained on page 252 this is probably due to less volatile chlorides of silicon which seem to be removed with considerable difficulty. The figures indicate, however, that the process of separation was still taking place even in the most carefully and elaborately distilled material, Sample III. In Sample IV the fractionation was many times as effective owing to the use of fractionating towers in nearly every distillation. The greater efficiency is obvious from the fact that even before the distillation was half completed, extreme fractions, Nos. 1 and 14, showed no indication of a difference in composition, and the uniformity of all the material from that point on is all that could be desired. There seems to be no question therefore that

the results of the analyses of Sample IV should be given preference to those of the first three samples of chloride.

The silicon tetrabromide, although distilled at the beginning of the fractional distillation without the use of fractionating columns, ultimately was repeatedly distilled in much the same way as Sample IV of the chloride. Here also uniformity in composition over a wide range of fractions was secured. The fact that the least volatile fraction, No. 8, gave a distinctly higher result than the remainder, is counterbalanced by the fact that the three residual fractions from distillations immediately following, were apparently no different from the more volatile fractions.

Furthermore, the fourth chloride series and the bromide series yielded almost identical results. Therefore the average of the mean values from these two series, 28.063, is the most probable value which can be derived from these data. It seems unlikely that further fractional distillation would have affected this outcome.

It is interesting to compare the influence which various impurities would have on the results. In the following table are given the effects produced upon the apparent atomic weight of silicon by one-tenth of one per cent of the more likely impurities.

| | | | |
|---|---|---|---|
| $Si_2Cl_6$ | +0.009 | $Si_2Br_6$ | +0.009 |
| $Si_3Cl_8$ | +0.014 | $Si_3Br_8$ | +0.014 |
| $Si_2OCl_6$ | +0.024 | HBr | −0.024 |
| HCl | −0.024 | $CBr_4$ | −0.016 |
| $CCl_4$ | −0.016 | $TiBr_4$ | +0.020 |
| $TiCl_4$ | +0.020 | | |

The bearing of the outcome of the foregoing work upon the isotopic character of silicon is an interesting one. Aston [26] finds ample evidence of the existence of two isotopes of this element, with masses 28 and 29. He then continues:

"The evidence of a silicon of atomic weight 30 is of a much more doubtful character. Its presence is suggested by the lines 30, 49, 68 and 87, but the possibility of hydrogen compounds makes the evidence somewhat untrustworthy, and no proof can be drawn from a second order line 15, as this is normally present and is due to $CH_3$. On the other hand, if we accept a mean atomic weight as high as 28.3, the relative intensity of the lines due to compounds of $Si^{28}$ and $Si^{29}$ indicates the probable presence of an isotope of higher mass."

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[26] Phil. Mag., **40**, 628 (1920).

It is obvious that the atomic weight derived in this paper is more nearly in accord with the evidence yielded by mass spectra as regards the proportion of the isotopic components of silicon, than the value 28.3 which has been in general use for some time. Assuming the existence of appreciable proportions of only the two isotopes 28 and 29, our result indicates that the ratio of lighter to heavier is about 14 to 1.

With at least two isotopes of silicon, chlorine, and bromine, there are evidently possible ten different tetrachlorides of silicon as well as ten different tetrabromides, with molecular weights ranging from 168, at intervals of one unit, to 177 in the case of the chloride, and from 344 to 353 in the case of the bromide. Of these, the two lightest, $Si^{28}(Cl^{35})_4$, 168, and $Si^{28}(Br^{79})_4$, 354, are presumably the most abundant and the most volatile.

The question therefore may be raised as to whether partial separation may have occurred during the fractionation of the two liquids.

If, however, separation actually occurs at all during the fractionation, it certainly is to be expected that it will continue to take place during the whole fractionation. The absence of any systematic difference in composition among the fractions analyzed in the case of Series IV and V, which covered a large proportion of the original material, is strong evidence that no important separation actually was taking place.

This is only to be expected from the fact that the conditions of distillation were far from ideal for the separation of isotopic substances, for as Mulliken and Harkins [27] and others have pointed out, such a separation is to be expected only when distillation takes place at extremely low pressures.

We are very greatly indebted to the Wolcott Gibbs and Bache Funds of the National Academy of Sciences for generous assistance in providing the necessary apparatus and materials.

## Summary.

1. Improved methods for fractional distillation out of contact with the air at various temperatures have been devised.

2. The analysis of pure silicon tetrachloride and tetrabromide has yielded the values 28.067 and 28.059 for the atomic weight of silicon. The average value is 28.063 (Ag = 107.880).

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[27] Jour. Amer. Chem. Soc., **44**, 143 (1922).